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Supplementary Information

Global Small-Angle X-ray Scattering Data Analysis of Triacylglycerols in the Molten State (Part I)

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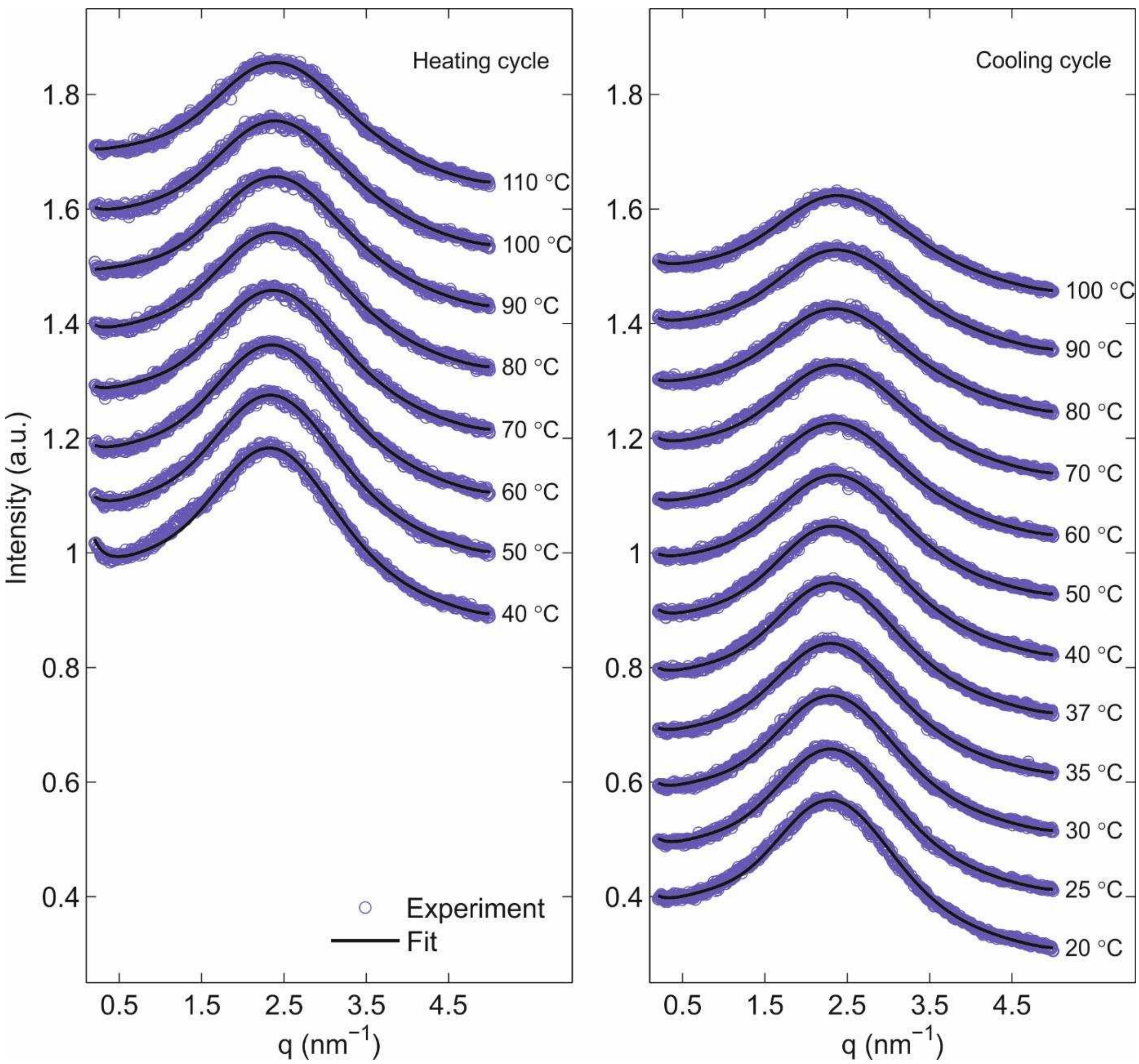

Figure S1. Global fitting of the molten CB with the 3-Gaussian TAG assembly model. (A) Heating ramp and (B) cooling ramp.

Transforming FWHM(q) into FWHM(z)

In this short paragraph we demonstrate, how to transform the FWHM(q) in the inverse space to the corresponding FWHM(z) in real space (cp. Equation 4):

$$FWHM(z) = \frac{2\pi}{q_c - FWHM(q)/2} - \frac{2\pi}{q_c + FWHM(q)/2}$$

$$FWHM(z) = \frac{2\pi\,(q_c + FWHM(q)/2)}{q_c^2 - (FWHM(q)/2)^2} - \frac{2\pi\,(q_c - FWHM(q)/2)}{q_c^2 - (FWHM(q)/2)^2}$$

$$FWHM(z) = \frac{2\pi\,FWHM(q)}{q_c^2 - (FWHM(q)/2)^2}$$

Dimensionality of TAG nanoclusters in the molten state

The overall decay rate of scattering intensity in the Guinier region can be used to evaluate the dimensionality of scattering aggregates on the nanometre scale. It is known that the 1D structures demonstrate a decay in the scattering intensity proportional to q^{-1}, while for 2D structures, the scattering intensity decays with q^{-2}. In our global analysis approach, the scattering form factor is corrected for 2D structures by applying the Lorentz correction of q^{-2} (see Eq. 6 in the main text). As argued in our paper, the formation of lamellar aggregates in the molten state of TAGs is very plausible as the nascent phase is the smectic, lamellar α-polymorph.

Despite this appealing argumentation, our current studies cannot exclude though, the presence of 1D structures at the early stages of crystallisation, such as core-shell rod-like assemblies (wormlike aggregates). In order to test this alternative interpretation of the SAXS data, we demonstrate that the experimental scattering intensity can also be simulated by applying the q^{-1} correction factor:

$$I(q) = \frac{|F(q)^2|}{q^1} \qquad \text{(SI.1)}$$

Figure S1, demonstrates the successful simulation of scattering curves by applying either of the two Lorentz corrections, q^{-1} and q^{-2}, respectively. First we note, that for the given the goodness of both fits (see Figure S1 A, B), we cannot statistically prefer one model to the other (lamellar versus wormlike). Secondly, note the resulting electron density profiles show slightly larger extensions in the 1D embedment.

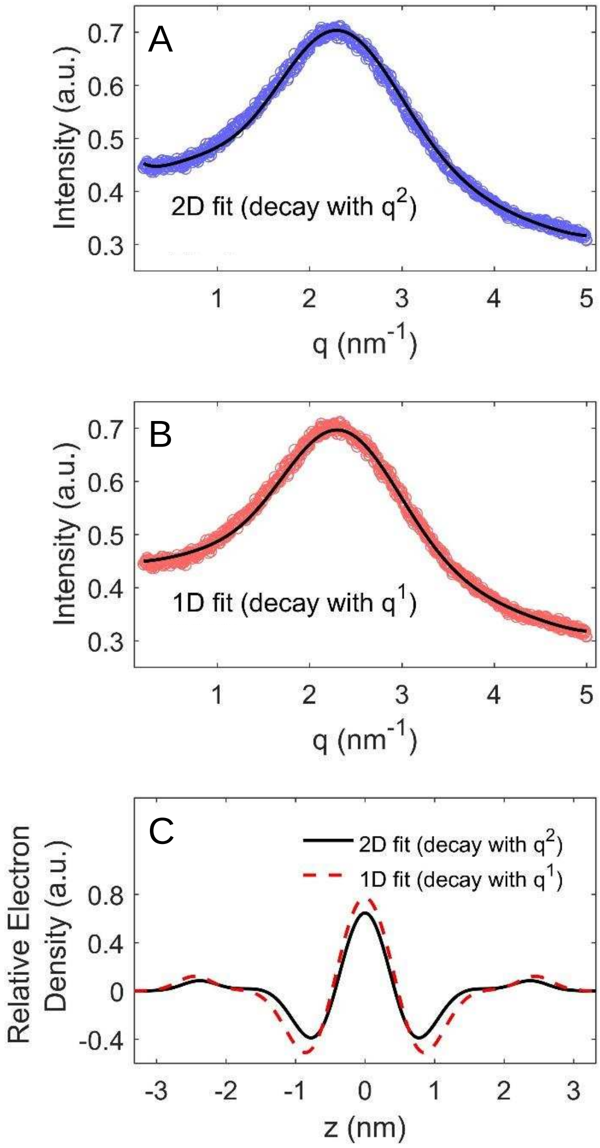

Figure S2. 3-Gaussian TAG assembly model tested for a 1D and 2D embedment. (A) The diffuse scattering of molten TAGs at 20 °C (just after completing the cooling ramp) is fitted with the 3G-electron-density profile model with an assumed idealized 2D embedment, i.e. this refers to a lamellar assembly model. (B)The same SAXS pattern fitted with the 3G-electron-density profile model with an assumed idealized 1D embedment, i.e., this refers to a wormlike assemblies. (C) Resulting electron density profiles resulting from the 3-Gaussian TAG assembly model tested for a 1D and 2D embedment, respectively.

Form factor discussion of plate-like particles

The form factor description of plate-like particles is fairly well known and goes back to works originally published by Porod [1] and Kratky and Porod [2] in 1948. For newer publication, we recommend two references from Glatter and co-workers [3, 4] as well as to study the appendix given by Nagle and collaborators in reference [5].

The particle factor or form factor squared $F(q)^2$ of lamellar or plate-like particles can be shown to be reduced to the description of the thickness or cross-sectional scattering function $F_t(q)^2$, when the cross-sectional thickness is much smaller than the extension in the other two dimensions [1-5]:

$$F(q)^2 = (2\pi A/q^2)\, F_t(q)^2$$

where $1/q^2$ is the so-called Lorentz corrections and A is the area of the basal plane. Note, in the main text $F_t(q)^2$ is written in short as $F(q)^2$.

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